

Charge fluctuations in the unconventional metallic state of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$

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Charge fluctuations in the quasi-one-dimensional material $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ are analyzed based on a multiorbital extended Hubbard model. A charge ordering transition induced by Coulomb repulsion is found with a charge ordering pattern different from a conventional charge density wave driven by Fermi surface nesting. The metallic state displays a characteristic charge collective mode which softens signalling the proximity to the transition. We argue that the strong scattering between electrons generated by these charge order fluctuations can lead to the unconventional metallic state observed above the superconducting transition temperature in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$.

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Introduction and motivation. Charge ordering phenomena is relevant to a wide range of strongly correlated materials including copper-oxide (high-temperature) superconductors[1–3], manganites[4], sodium cobaltates [5] and the layered quarter-filled organic molecular conductors[6]. In particular, for the cuprate superconductors charge ordering has been recently observed in the pseudogap region in close proximity to the superconducting phase raising questions about its relevance to the high- T_c superconductivity[7].

The purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ is a quasi-one-dimensional material which displays behavior consistent with a Luttinger liquid [8, 9] in a wide temperature range. When temperature is decreased an upturn of the resistivity occurs at $T_m \sim 20$ K and the material becomes superconducting at lower temperatures around $T_c \sim 1$ K [10]. The rather small enhancement of the resistivity below T_m (just a factor of two) and the lack of spectral evidence of a gap makes it difficult to reconcile this upturn with an insulating phase. The fact that the resistivity is a decreasing function of temperature above the superconducting transition is in contrast with the superconducting transition observed in conventional metals and in other strongly correlated materials except for the quarter-filled organic materials[11, 12]. Understanding the unconventional metallic state, whether it is a "bad" metal with incoherent excitations or not, may be crucial to the mechanism of superconductivity in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$.

Conventional charge density waves (CDW) in solids involve a modulation of the electronic density accompanied by a crystal structure distortion. In $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ the resistivity upturn below T_m is not accompanied by any structural transition as evidenced by high resolution X-ray scattering, neutron scattering,[20] and thermal expansion[21] experiments. However, observing a structural instability driven by Fermi surface nesting re-

quires a sufficiently large electron-lattice coupling which may not be present in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ as is also found in the family of quasi-one-dimensional TMTTF organic salts [13].

In this Letter, we present a microscopic theory for the unconventional metallic properties observed in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. Based on a minimal extended Hubbard model recently introduced[14, 15] we show that $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ is close to a charge ordering (CO) transition driven by the Coulomb repulsion. Using the random phase approximation (RPA), we identify the CO pattern characterized by the ordering wave vector, \mathbf{Q} , which is different from the conventional $2k_F$ -CDW. The CO transition line, T_{CO} , displays 'reentrant' behavior which is responsible for a non-monotonic behavior of charge fluctuations being strongest around T_m in the metallic phase close to CO. The dynamical charge susceptibility displays a collective mode softening at momentum \mathbf{Q} signalling the proximity to CO. We propose measurements of the dielectric constant [16], scanning tunneling microscopy (STM) and nuclear magnetic resonance (NMR) relaxation rate, $1/T_1T$, to probe the T -dependence, strength and CO pattern of charge fluctuations in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, testing our predictions. The charge collective mode in the metallic phase can be explored with high resolution inelastic X-ray scattering (HRIX). In analogy with the effect of magnetic fluctuations in nearly antiferromagnetic metals, charge fluctuations can also lead to the unconventional T -dependence of the specific heat coefficient[10] and resistivity [17, 18] observed in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ assuming that the material is in the proximity but not necessarily at CO.

Microscopic model. In Fig. 1 we show the zig-zag ladders consisting of Mo and O atoms which lead to the characteristic quasi-one-dimensional electronic structure of the material. The minimal strongly correlated model

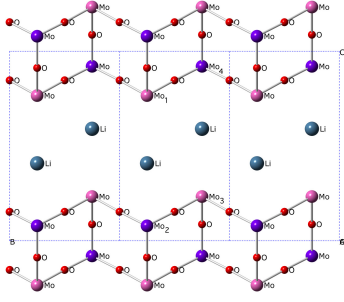


FIG. 1: (Color online) Charge ordering phenomena in the extended Hubbard model (1) for $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. We show the crystal structure of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ projected onto the b - c plane showing only the Mo and O atoms forming the zig-zag ladders relevant to the low energy electronic properties. The real space charge ordering pattern consisting of alternating charge-rich (purple) and charge-poor (magenta) Mo atoms arising in the model is also shown.

which can capture the essential physics of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ is a multi-orbital extended Hubbard model [14] which reads:

$$H = H_0 + H_U, \quad (1)$$

where H_0 is the non-interacting tight-binding Hamiltonian: $H_0 = \sum_{i\alpha,j\beta} t_{i\alpha,j\beta} (d_{i\alpha\sigma}^\dagger d_{j\beta\sigma} + c.c.)$, where $d_{i\alpha\sigma}^\dagger$ creates an electron with spin σ in a d_{xy} orbital of a Mo atom, α , which runs over four Mo atoms in the unit cell i as shown in Fig. 1. The one-electron hamiltonian can be expressed in terms of Bloch waves: $H_0 = \sum_{\mathbf{k}\alpha\beta\sigma} t_{\alpha\beta}(\mathbf{k}) d_{\mathbf{k}\alpha\sigma}^\dagger d_{\mathbf{k}\beta\sigma}$ with the following non-zero matrix elements[14]: $t_{12}(\mathbf{k}) = t_{34}(\mathbf{k}) = -t_\perp e^{i\mathbf{k}\cdot\delta_\perp}$, $t_{13}(\mathbf{k}) = -2t' e^{i\mathbf{k}\cdot\delta_1} \cos(\frac{\mathbf{k}\cdot\mathbf{b}}{2})$, $t_{14}(\mathbf{k}) = -2tA(k_a, k_c) \cos(\frac{\mathbf{k}\cdot\mathbf{b}}{2})$, $t_{23}(\mathbf{k}) = -2tA(k_a, k_c) \cos(\frac{\mathbf{k}\cdot\mathbf{b}}{2})$, where $A(k_a, k_c) = e^{-i2\pi[0.1602k_a + 0.1542k_c]}$, $\delta_\perp = 0.17\mathbf{a} - 0.31\mathbf{c}$ and $\delta_1 = 0.01\mathbf{a} + 0.53\mathbf{c}$. The momentum is expressed in terms of the unit cell coordinate system:

$\mathbf{k} = k_a\mathbf{a} + k_b\mathbf{b} + k_c\mathbf{c}$, and the hopping parameters are taken as: $t = 0.5$ eV, between the nearest-neighbor Mo_1 - Mo_4 and Mo_2 - Mo_3 atoms along a chain, $t_\perp = -0.024$ eV between Mo_1 - Mo_2 or Mo_3 - Mo_4 atoms in a rung of a ladder and $t' = 0.036$ eV between Mo_1 - Mo_3 atoms in neighboring zig-zag ladders (see Fig. 1). The diagonalized hamiltonian: $H_0 = \sum_{\mathbf{k}\mu\sigma} \epsilon_\mu(\mathbf{k}) d_{\mathbf{k}\mu\sigma}^\dagger d_{\mathbf{k}\mu\sigma}$, leads to four bands denoted by μ , the two lowest ones crossing the Fermi energy[14, 19]. The Fermi surface close to one quarter-filling, $n = 0.45$, is shown in Fig. 2 (a).

The Coulomb interaction terms in the hamiltonian have been described previously in [14, 15] and read:

$$H_U = \sum_{i\alpha,j\beta} U_{i\alpha,j\beta}^{i\alpha,j\beta} n_{i\alpha} n_{j\beta}. \quad (2)$$

This term only includes the density-density Coulomb interaction contributions included in the extended Hubbard model. The Coulomb matrix elements in momentum space, $U_{\alpha\beta}^{\gamma\delta}(\mathbf{q}) = U_{\alpha\beta}^{\alpha\beta}(\mathbf{q}) \delta_{\alpha\gamma} \delta_{\beta\delta}$, have analogous expressions to the hopping terms but with the diagonal Coulomb energies, $U_{\alpha\alpha}^{\alpha\alpha}(\mathbf{q}) = U/2$. Here, we only consider the nearest-neighbor Coulomb interactions, $V = V_\perp$, within the zig-zag ladders which leads to the CO pattern in Fig. 1.

Multiorbital RPA approach. The above model is analyzed based on a multi orbital random phase approximation (RPA) approach. The RPA charge susceptibility reads[24]:

$$(\chi_c)_{lm}^{np}(\mathbf{q}, i\omega) = (\chi_0)_{lm}^{np}(\mathbf{q}, i\omega) - \sum_{uvwz} (\chi_c)_{uv}^{np}(\mathbf{q}, i\omega) (U_c)_{wz}^{uv}(\mathbf{q}) (\chi_0)_{lm}^{wz}(\mathbf{q}, i\omega), \quad (3)$$

where the indices l, m, n, p refer to the four Mo d_{xy} orbitals present in the unit cell. $\hat{U}_c(\mathbf{q})$ is the Coulomb matrix appearing in Eq. (2) expressed in momentum space. The non-interacting susceptibility, χ_0 , reads:

$$(\chi_0)_{lm}^{wz}(\mathbf{q}, i\omega) = -\frac{2}{N} \sum_{\mathbf{k}, \mu, \nu} \frac{a_\mu^l(\mathbf{k}) a_\mu^{w*}(\mathbf{k}) a_\nu^m(\mathbf{k} + \mathbf{q}) a_\nu^{z*}(\mathbf{k} + \mathbf{q})}{i\omega + \epsilon_\nu(\mathbf{k} + \mathbf{q}) - \epsilon_\mu(\mathbf{k})} [f(\epsilon_\nu(\mathbf{k} + \mathbf{q})) - f(\epsilon_\mu(\mathbf{k}))], \quad (4)$$

where N is the number of lattice sites, ν, μ are band indices. The matrix elements $a_\mu^l(\mathbf{k}) = \langle l | \mu \mathbf{k} \rangle$ are the coefficients of the eigenvectors diagonalizing H_0 .

Charge ordering transition. In Fig. 2 we show the evolution of the static RPA charge susceptibility obtained from: $\chi_c(\mathbf{q}) = \sum_{uv} (\chi_c)_{uv}^{uu}(\mathbf{q}, i0^+)/2$, with the offsite Coulomb repulsion V and $U = 1$. The susceptibility is evaluated along the $(0, \frac{q}{b}, \frac{\pi}{c/2})$ direction in mo-

mentum space. The charge susceptibility is enhanced with V particularly at the wave vector $\mathbf{Q} = (0, \frac{\pi}{b/2}, \frac{\pi}{c/2})$, which corresponds to having alternating charge rich and charge poor Mo atoms shown in Fig. 1. This signals the charge ordering transition associated with the Coulomb repulsion (note that the unit cell defined by a, b, c contains four Mo atoms). There is a smaller structure at about $(0, \frac{\pi}{b}, \frac{\pi}{c/2})$ associated with the nesting vector $2k_F$

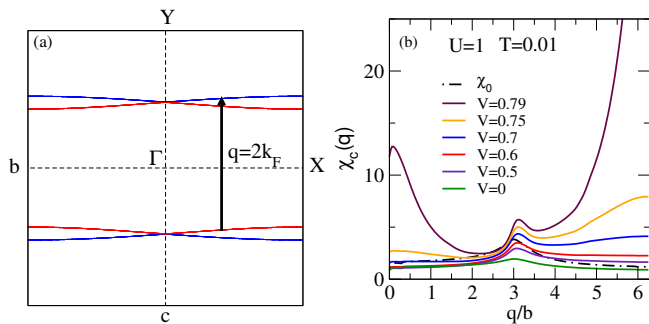


FIG. 2: (Color online) Charge order instability induced by Coulomb repulsion. (a) The Fermi surface obtained from our effective model for $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ is shown. (b) The static charge susceptibility, $\chi_c(\mathbf{q})$ along the $(0, \frac{q}{b}, \frac{\pi}{c/2})$ direction shows the rapid increase of charge fluctuations at wave vector: $\mathbf{Q} = (0, \frac{\pi}{b/2}, \frac{\pi}{c/2})$ associated with the Coulomb induced CO occurring at $V_{\text{CO}} \approx 0.8$. The smaller structure at $\mathbf{q} = (0, \frac{\pi}{b}, \frac{\pi}{c/2})$ is related to Fermi surface nesting at $q = 2k_F \lesssim \pi/b$.

connecting the different sections of the Fermi surface as shown in Fig. 2.

Phase diagram. The $T - V$ phase diagram obtained from the present RPA approach is shown in Fig. 3. The metallic and charge ordered (CO) phases shown in Fig. 1 are separated by a 'reentrant' charge ordering transition line T_{CO} . In the metallic phase, close to CO, charge fluctuations with the \mathbf{Q} wave vector are strongly enhanced as shown in the inset of Fig. 4 for $V = 0.68$ around our proposed location of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ in the phase diagram. An enhancement of the low energy spectral weight occurs leading to a charge collective mode which softens and increases in amplitude as T is decreased from about $T = 0.6$. Such T -dependence of the charge collective mode occurs down to T_m , at which this behavior is reversed, *i. e.* the collective mode hardens following the 'reentrant' shape of the transition line T_{CO} . Thus, T_m is the temperature scale at which charge fluctuations induced by Coulomb repulsion are strongest in the homogeneous metallic phase sufficiently close to CO.

Close to the charge ordering instability, the electronic scattering by dynamical charge fluctuations[26] largely influence the normal metallic properties. In analogy with nearly antiferromagnetic two-dimensional metals the scattering rate is non Fermi liquid, $1/\tau(T) \propto T$, with a crossover [27] to Fermi liquid behavior $1/\tau(T) \propto T^2$ below the temperature T^* (as obtained in Ref. [27]). The temperature T^* drops to zero close to the transition. Our results are compatible with Luttinger liquid physics at higher temperatures although describing the crossover from one NFL to the other requires more sophisticated theoretical tools. We also expect that the particular T -dependence of the charge fluctuations, leads to resistivity and specific heat slope [10] enhancements around T_m . Furthermore, we find that the phase dia-

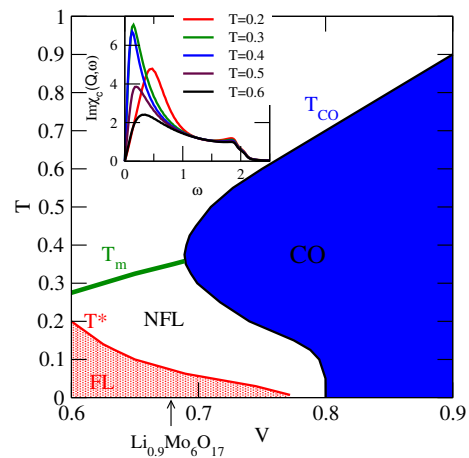


FIG. 3: (Color online) Phase diagram of the effective extended Hubbard model for $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. The $T - V$ phase diagram obtained from RPA is shown for fixed value of $U = 1$ and varying V . Charge ordered (CO) and homogeneous metallic phases are separated by the CO transition line, T_{CO} , which displays 'reentrant' behavior. T_m is the temperature scale associated with the onset of charge fluctuations. Fermi liquid (FL) and non Fermi liquid (NFL) phases are separated by the crossover scale T^* . The inset shows the T -dependence of $\text{Im}\chi_c(\mathbf{Q}, \omega)$ in the metallic phase close to CO displaying the softening and enhancement of the charge collective mode around T_m . The proposed location for $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ at ambient pressure is marked with a vertical arrow. The system would effectively shift to smaller V under the effect of pressure.

gram in Fig. 3 qualitatively agrees with the key features of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. Under an external pressure, the temperature for the resistivity upturn, T_m , is suppressed [17], whereas the crossover temperature, T^* , for Fermi liquid behavior increases. The observed behavior of T_m and T^* with pressure is consistent with the phase diagram shown in Fig. 3, since applying pressure is equivalent to reducing V in our model. Electronic localization effects arising close to CO not included in the present approach should lead to strong suppression of transition temperatures and T_m .

Softening of charge collective mode close to CO. In Fig. 4 we analyze $\text{Im}\chi_c(\mathbf{q}, \omega)$ as the system is driven close to CO at low temperature $T = 0.05$. For non-interacting electrons, $U = V = 0$, spectral weight is found in the particle-hole continuum with small weight in the region between 0 and $2k_F$ as expected for quasi-one-dimensional systems. Once the on-site Coulomb repulsion is turned on spectral weight is enhanced around the highest energy branch of the particle-hole continuum due to particle-hole excitations promoted by U . As V is increased a redistribution of charge spectra around \mathbf{Q} occurs in which particle-hole excitations of lower and lower energies gain weight. At $V = 0.68$ a collective charge fluctuation mode is clearly Close to the CO transition, $V \lesssim V_{\text{CO}}$, the collective mode amplitude increases shifting to zero energy

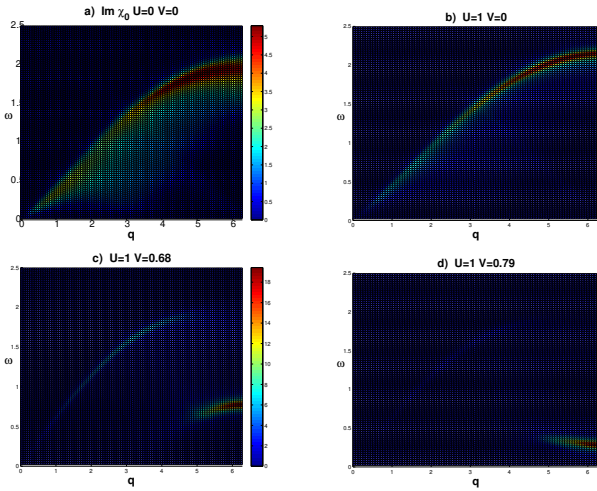


FIG. 4: (Color online) Imaginary part of the charge susceptibility $\text{Im}\chi_c(q, \omega)$ showing the emergence and softening of the collective excitation as the interaction increases. a) Noninteracting charge susceptibility $\text{Im}\chi_0(q, \omega)$ displaying the particle-hole continuum b) a Hubbard-like interaction ($U = 1, V = 0$) c) an interaction compatible with purple bronze phenomenology $U = 1, V = 0.68$ and d) close to the CO transition $U = 1, V = 0.79$. Temperature is $T = 0.05$.

signalling the Coulomb driven CO transition. The behavior found for $\text{Im}\chi_c(\mathbf{q}, \omega)$ close to CO can be understood from the singular part of the charge susceptibility in a two-dimensional system: $\chi_c(\mathbf{q}, \omega) \approx \frac{A}{i\omega - \omega_{\mathbf{q}}}$, with $\omega_{\mathbf{q}} = \omega_0 + C|\mathbf{q} - \mathbf{Q}|^2$, where $\omega_0 \rightarrow 0$ as the CO boundary is approached[26] and C a positive constant.

The dynamical charge response of the system, $\text{Im}\chi_c(\mathbf{q}, \omega)$, can be experimentally analyzed using HRIX. In particular, the dispersion of the collective mode discussed above around \mathbf{Q} could be extracted probing the proximity of the system to CO. Analogous plasmon softening around $2k_F$ has been observed with inelastic electron scattering on materials driven close to a conventional charge density wave [28] instability. Measurements of the real part of the dielectric constant of the material could also track the enhancement in charge fluctuations occurring around T_m as has been done in quasi-one-dimensional organic systems.[16].

Concluding remarks. We propose a new framework to describe the anomalous metallic behavior of the quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ at the temperatures $T \approx T_m$ around the resistivity upturn. The small resistivity enhancement accompanied with a weak feature on the specific heat are not consistent with an insulating state. There are neither signatures of a structural distortion nor convincing evidence of another phase transition. Our analysis shows that these anomalies can be attributed to strong charge fluctuations associated with CO induced by Coulomb repulsion and manifest themselves through a low energy collective excitation. Experimental probes

such as NMR- $1/T_1T$ relaxation rate, HRIX, STM and measurements of the dielectric constant can be used to search for fingerprints of such CO fluctuations.

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- [1] G. Ghiringhelli, *et al.*, Science **377** 821, (2012).
 - [2] E. H. da Silva Neto, *et al.*, Science **343** 393 (2014).
 - [3] R. Comin, *et al.*, Science **343** 390 (2014).
 - [4] S. Mori, C. H. Chen, and S.-W. Cheong, Nature **392**, 473 (1998).
 - [5] N. P. Ong and R. J. Cava, Science **305**, 52 (2004); M.-L. Foo, *et al.*, Phys. Rev. Lett. **92**, 247001 (2004).
 - [6] H. Seo, J. Merino, H. Yoshioka, and M. Ogata, Jour. Phys. Soc. Jap. **75**, 051009 (2006).
 - [7] E. Fradkin and S. Kivelson, Nat. Phys. **8**, 864 (2012).
 - [8] F. Wang, *et al.*, Phys. Rev. Lett. **96**, 196403 (2006); F. Wang, *et al.*, Phys. Rev. Lett. **103**, 136401 (2009); L. Dudy, *et al.*, Jour. of Phys. Cond. Mat. **25**, 014007 (2013).
 - [9] J. Hager, *et al.*, Phys. Rev. Lett. **95**, 186402 (2005).
 - [10] C. Schlenker, *et al.*, Physica B **135** 511 (1985).
 - [11] N. Morinaka, *et al.*, Phys. Rev. B **80**, 092508 (2009).
 - [12] S. Kaiser, *et al.*, Phys. Rev. Lett. **105**, 206402 (2010).
 - [13] D. S. Chow, *et al.*, Phys. Rev. Lett. **85** 1698 (2000).
 - [14] J. Merino and R. H. McKenzie, Phys. Rev. B **85**, 235128 (2012).
 - [15] P. Chudzinski, T. Jarlborg, and T. Giamarchi, Phys. Rev. B **86**, 075147 (2012).
 - [16] F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, J. Phys.: Condens. Matter **12**, L435 (2000); P. Monceau, Adv. Phys. **61**325 (2012).
 - [17] C. Escribe Filippini, *et al.*, Physica C **162**164, 427 (1989).
 - [18] N. Wakehman, *et al.*, Nat. Comm. **2**, 396 (2011).
 - [19] Z. S. Popović and S. Satpathy, Phys. Rev. B **74** 045117 (2006); M.-H. Wangbo and E. Canadell, J. Am. Chem. Soc. **110**, 358 (1988).
 - [20] M. S. da Luz, J. J. Neumeier, C. A. M. dos Santos, B. D. White, H. J. I. Filho, J. B. Leao, and Q. Huang, Phys. Rev. B **84**, 014108 (2011).
 - [21] C. A. M. dos Santos, B. D. White, Y. K. Yu, J. J. Neumeier, and J. A. Souza, Phys. Rev. Lett. **98**, 266405 (2007).
 - [22] M. Onoda, K. Toriumi, Y. Matsuda, and M. Sato, J. Solid State Chem. **66**, 163 (1987).
 - [23] T. Jarlborg, P. Chudzinski, and T. Giamarchi, Phys. Rev. B **85**, 235108 (2012).
 - [24] S. Graser, T. A. Maier, P. J. Hirschfeld, and D. J. Scalapino, New Jour. Phys **11**, 025016 (2009).
 - [25] M. Z. Hasan, *et al.*, Phys. Rev. Lett. **88** 177403 (2002).
 - [26] C. Castellani, C. Di Castro, and M. Grilli, Phys. Rev. Lett. **75** 4650 (1995).

- [27] J. Merino, A. Greco, N. Drichko, and M. Dressel, Phys. Rev. Lett. **96** 216402 (2006).
- [28] Jasper van Wezel, *et. al.*, Phys. Rev. Lett. **107** 176404 (2011).